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Sampling Semivolatile Organic Compounds in Indoor Air

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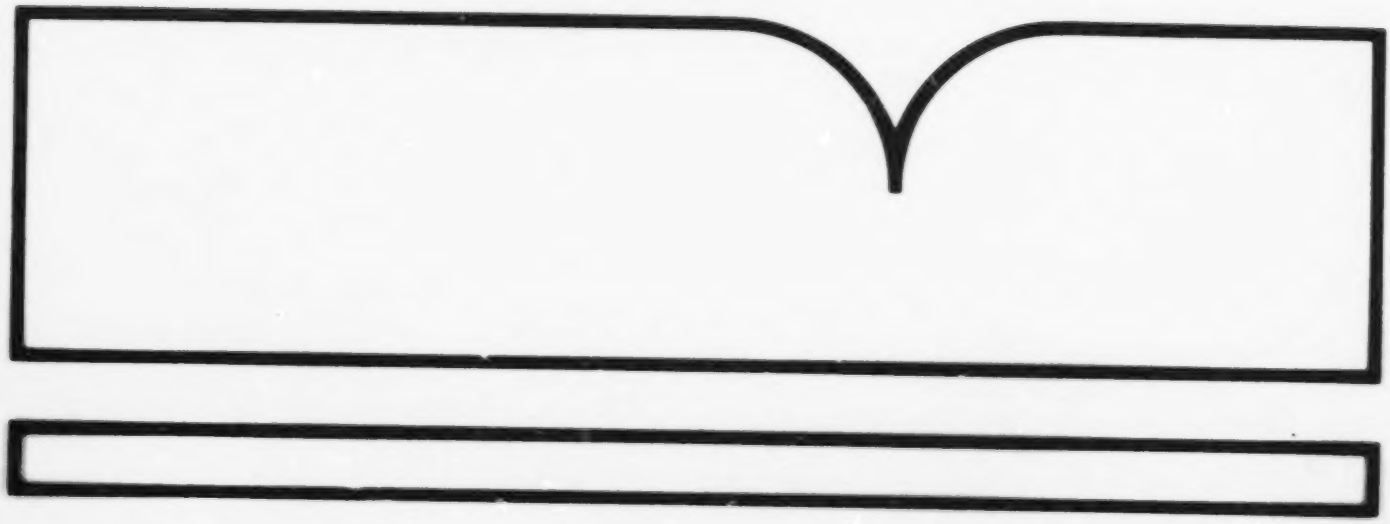

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Semivolatile organic compounds (SVOCs) are distributed in air between the particulate and the vapor phases. Samplers for SVOCs in indoor air must therefore collect both airborne particles and vapors. We developed two prototype indoor samplers for SVOCs. Both are quiet, transportable, and operate entirely within the sampled environment. We evaluated their performance and estimated the ranges of indoor SVOC concentrations in four small indoor air studies.

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SAMPLING SEMIVOLATILE ORGANIC COMPOUNDS IN INDOOR AIR

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Semivolatile organic compounds (SVOCs) are distributed in air between the particulate and the vapor phases. Samplers for SVOCs in indoor air must therefore collect both airborne particles and vapors. We developed two prototype indoor samplers for SVOCs. Both are quiet, transportable, and operate entirely within the sampled environment. We evaluated their performance and estimated the ranges of indoor SVOC concentrations in four small indoor air studies.

INTRODUCTION

We have done several small studies to evaluate newly developed sampling and analysis methods for polycyclic aromatic hydrocarbons (PAH) and other SVOCs [compounds with vapor pressures in the approximate range 10^{-2} to 10^{-8} kPa (10^{-1} to 10^{-7} torr)] in indoor air. To aid in the design of large-scale studies, we measured the concentration ranges of selected PAH and estimated the influences of several indoor PAH sources. Ten homes or fewer were sampled in each study. In our early studies, stratification variables included smoking, fireplace operation, and gas or electric heat and cooking. Because smoking overwhelmed the contributions of other indoor SVOC sources, we eliminated it from the later studies.

MATERIALS AND METHODS

Samplers. Initially, we collected indoor air samples for use in development of a new microbioassay (1) as well as for chemical analysis. The competing requirements of sufficiently large samples for bioassay, sufficiently small disturbances of air flows in the house, and minimum disturbance of the occupants by sampler noise led us to use a standard PS-1 sampling head (General Metal Works, Cleves OH), which holds a 10-cm quartz fiber filter followed by a Pyrex cartridge (60 mm i.d. x 125 mm) holding polyurethane foam (PUF) adsorbent (2). Vacuum tubing led from the sampling head through a window port to the pump, which was located outdoors in a sound-insulated box. Sufficient material for microbioassay was collected in 8 hr, sampling at approximately 200 L/min (7.2 cfm). Less time is needed for low levels of PAH, PCBs, and pesticides (3).

Although the above sampling system performed satisfactorily, the intrusive and unique modifications required to set up the sampling system in each individual house and other problems led to the development of a self-contained indoor SVOC sampler. It incorporates the PS-1 sampling head. The pump, an Amtex bypass vacuum motor 116100-00 (Ametek, Lamb Electric Division, Kent OH), is in an acoustically insulated box. The box reduces the noise below NC-35, an acceptable value for a sleeping room (4). The nominal operating flow rate is 8 cfm. Venting to the outside is

not required in most cases (5). This quiet sampler has been used successfully in three separate studies. A PM-10 inlet (3) and a compound annular denuder to allow phase distribution studies (6) were also designed and built for this sampler.

We also developed a similar, smaller indoor sampler for sampling for chemical analysis only (7). It operates at approximately 20 L/min and likewise incorporates a filter (47 mm) and a sorbent cartridge. The cartridge holds up to 30 g of XAD-2 resin and can be placed entirely within a Soxhlet extractor. The original design included acoustic insulation and vibration isolation mounts for noise reduction, a carbon vane pump, a flow transducer for measurement of the flow rate, a seven-day programmable timer, a data logger, vents and a cooling fan. The entire package is the size of a small suitcase (51 x 35 x 21 cm) and is readily portable. Sufficient material for chemical analysis of many SVOCs can be obtained in about two hours. To collect nitro-PAH, oxygenated PAH, and other less abundant SVOCs, sampling for eight to twelve hours is necessary.

Sorbents. A number of sorbents can be used to collect vapor-phase SVOCs. We originally used PUF, which has low resistance to air flow and has been validated for the collection of pesticides (8). However, it does not collect or retain well PAH with fewer than four rings or other similar compounds. Additionally, the PUF sample extracts gave widely varying results in microbioassay compared to extracts from other sorbents. In all but one (9) of our later studies, we used XAD-2 resin (Rohm and Hass, Philadelphia PA). Non-polar two-ring and larger aromatic compounds and most of the more polar aromatic derivatives are efficiently collected and retained on XAD-2 (10). To collect simultaneously both PAH and nicotine or other small SVOCs, XAD-4 resin, which is chemically similar to XAD-2, but with smaller pores, hence greater surface area, has proved to be superior (9).

Analysis. Because the SVOCs are distributed between the gaseous and particulate phases in air, both particles and vapor must be collected and analyzed to determine the true concentrations. Although filters and sorbents can be analyzed separately, the quantitative results reported separately would ignore the changes in the amounts on the filters and sorbents due to revolatilization or other sampling artifacts. These changes can be large; in some cases the artifact that results from revolatilization is of the same magnitude as the amount originally in the gas phase (11). Therefore, we generally extract each filter-sorbent pair together and report the total concentrations. Extraction solvents are usually 5% ether/hexane for PUF, and dichloromethane (DCM) for XAD-2 or XAD-4. To remove nicotine and PAH from XAD-4, we extract sequentially with ethyl acetate and DCM. Benzene/methanol is effective for polar analytes (12). Significant contamination of the indoor air by DCM or other solvent used to clean the XAD before use can occur. Residual DCM can be removed by fluidizing the resin in a stream of pure nitrogen gas while heating at 40 C (13).

We used GC/MS rather than HPLC for the PAH analyses, because it requires little clean-up and is therefore more cost-effective. To achieve the highest sensitivity, we used positive chemical ionization (PCI) GC/MS for the target PAH. For the nitro-PAH and other electrophilic compounds, we used negative CI GC/MS.

RESULTS AND DISCUSSION

Performance of the 20 L/Min Sampler. The performance of the 200 L/min sampler has been described elsewhere (2, 3, 5); thus we discuss only the 20 L/min sampler. Operation in the laboratory at ambient temperatures from 20 to 27 C raised the temperature inside the sampler as high as 38 C, but did not raise the temperature of the sampling inlet and caused no problems. Continous sampling over a 7-day period gave results equivalent to those obtained over seven consecutive 24-hr sampling periods, with the exception of reactive PAH or reaction products such as 9-fluorenone, 9-nitroanthracene, and pyrene carboxaldehyde (7).

Recently, we evaluated the performance of this sampler inside and outside five California homes as part of a larger pre-pilot study. Unexplained gaps in the recorded flow rates, although normal flow calibrations were obtained before, after, and during the experiments, indicated that recording flow controllers should be used instead of flow transducers, despite the higher cost. The thermal cut-off switches were set at 140 F; although satisfactory in the laboratory and inside residences, this setting was too low for outdoor operation in southern California. However, overall operation was satisfactory (14), and sufficient material was collected. Minor modification of the 20 L/min sampler should provide a relatively inexpensive, generally useful sampler for indoor SVOCs.

Target Compound Concentrations. The ranges and typical values of PAH concentrations in the homes that we sampled in California and in the three previous studies, in Columbus, Ohio, are shown in Tables 1 and 2. Statistical analysis (15, 16) showed that results were consistent from study to study, although we sampled different homes and used different sampling systems. An exception is that break-through of the smaller PAH and other small non-polar compounds occurred with PUF. Thus PUF is inappropriate as a back-up adsorbent for PAH or similar SVOCs.

In homes where smoking occurred, its effects dominated the results, with typical increases in PAH concentrations over non-smoking homes by a factor of three or more. The use of natural gas for heating and cooking also produced a small but statistically significant increase in indoor SVOCs. Indoor concentrations generally exceeded those outdoors.

Although fireplace use did not appear to have a statistically significant effect on indoor PAH levels, a reanalysis of the data using pattern recognition techniques showed that homes with fireplaces cluster and score strongly in the principal components that represent the more volatile SVOCs associated with wood combustion (17). Using pattern recognition may allow us to glean additional information from such studies.

The PAH and PAH derivative levels in the five California homes, where no heating systems were in operation, were slightly lower than those obtained in the Columbus, Ohio homes, most of which were studied in the winter heating season. Exceptions were some compounds associated with mobile sources, such as cyclopenta[c,d]pyrene, benzo[g,h,i]perylene and coronene, which were higher both inside and outside the California homes.

Marker Compounds. Quinoline concentrations paralleled those of nicotine in all homes. For separation of the contributions of various indoor pollutant sources, quinoline appears to be a useful marker compound for the presence of environmental tobacco smoke. It also simplifies both sampling (separate samplers for quinoline and PAH are not required) and analysis (GC/MS dynamic range problems are eliminated) compared to nicotine (9).

We were interested in finding one or more abundant compounds that could indicate the concentrations of less abundant, but potentially hazardous, PAH and PAH derivatives. The concentrations of three abundant PAH: phenanthrene, pyrene, and fluoranthene, were highly correlated with concentrations of such compounds as benzo[a]pyrene and benzo[g,h,i]perylene. Pyrene was most suitable, with a mean r^2 of 0.45 for individual compounds.

In several homes that had different indoor sources and widely varying concentrations of PAH, the concentration of phenanthrene remained at approximately 70% of the total PAH load. Thus phenanthrene may be a good marker for overall PAH concentration. We are investigating this possibility further.

CONCLUSIONS AND RECOMMENDATIONS

To sample PAH and other SVOCs in indoor air, a sampler incorporating a quartz fiber filter and XAD-2 or XAD-4 resin is generally useful. For chemical analysis only, a flow rate of 20 L/min provides adequate samples for most compounds in 8-12 hr.

Concentrations of PAH and related compounds in indoor air vary widely, from a few pg/m^3 to several hundred ng/m^3. The overall levels are much higher in homes occupied by smokers. Other influences on the PAH levels are more subtle. Use of gas heating systems (vented) and cooking appliances appears to increase the PAH levels. Spatial variability within a given home was small and not statistically significant. The effects of fireplace operation were not statistically significant, but could be observed using pattern recognition techniques. Further studies are necessary to determine the influences of gas versus electric home heating and cooking, of other indoor sources, and to define the day-to-day variability. These studies should be done in the absence of smoking.

The abundant compounds fluoranthene, pyrene, and phenanthrene show promise as predictors of the levels of the other target PAH, such as benzo[a]pyrene, which occur at levels that are several orders of magnitude lower. Pyrene is the best marker compound for most of the individual target compounds investigated (15). Phenanthrene may be useful to indicate total PAH load.

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TABLE 1. INDOOR CONCENTRATION RANGES OF SELECTED PAH, ng/m^3

Compound	Lowest	Highest
Quinoline	0.29	1100
Phenanthrene	11.0	210
Fluoranthene	2.42	23.0
Pyrene	1.5	18.1
Cyclopenta[c,d]pyrene	0.00	2.00
Benz[a]anthracene	0.085	3.40
Chrysene	0.18	7.20
Benzofluoranthenes	0.18	5.83
Benzo[a]pyrene	0.00	3.33
Indeno[1,2,3-c,d]pyrene	0.00	2.60
Benzo[g,h,i]perylene	0.00	4.5
Coronene	0.00	3.7
1-nitropyrene	0.02	0.28
2-nitrofluoranthene	0.01	0.02

TABLE 2. TYPICAL AVERAGE PAH CONCENTRATIONS IN HOMES, ng/m^3

	Smoking	Non-smoking	
	Gas Heat	Electric Heat	Gas Heat
Compound	Gas Stove	Electric Stove	Gas Stove
Quinoline	240	3.1	2.8
Phenanthrene	87	19	31
Fluoranthene	8.6	2.99	3.7
Pyrene	5.2	2.13	2.8
Cyclopenta[c,d]pyrene	1.1	0.17	0.21
Benz[a]anthracene	1.4	0.20	0.46
Chrysene	2.6	0.37	0.67
Benzofluoranthenes	2.5	0.47	0.93
Benzo[a]pyrene	1.2	0.28	0.63
Indeno[1,2,3-c,d]pyrene	0.97	0.32	0.82
Benzo[g,h,i]perylene	1.4	0.53	0.88
Coronene	0.60	0.52	1.3
1-Nitropyrene	0.044	0.027	0.029
2-Nitrofluoranthene	0.052	0.018	0.033